Review of Advanced Technologies for Removing TBT from Ship Washdown and Shipyard Runoff Wastewaters

Michael A. Champ[1] Gary C. Schafran[2], and Thomas J. Fox[3],

Abstract

A project funded by the Office of Naval Research held a series of special sessions at the Oceans 99 Conference in Seattle, Washington. The purpose of this project is to identify and review available international advanced technologies that can be used to achieve a reduction in wastewaters discharged from shipyards and drydocks that range from several thousand to several hundred thousand parts-per-million (ng/L) to less than 50 ng/L to protect marine resources in rivers, bays and estuaries.

Keywords:

Tributyltin (TBT), Discharges, NPDES Permit, Washdown, Shipyard Wastewaters, Advanced Waste Treatment, Carbon, DAF.

Introduction

TBT is highly toxic to some aquatic organisms at concentration levels measured in parts-per-trillion (ng/L). While it is used in a wide variety of industrial and commercial products, of most concern is its use in antifouling paints for ship hulls. Tributyltin was introduced as a biocide in antifouling paints over 30 years ago. It is said to be the most toxic material ever introduced deliberately by mankind into the marine environment.

In 1997, after 10 years of study, the United States Environmental Protection Agency proposed a national saltwater aquatic life criterion for TBT of 10 ng/L (62 CFR 42554, August 7, 1997). The Commonwealth of Virginia led the nation in developing a TBT standard, establishing in 1987, a surface water standard of just 1 ng/L and an NPDES discharge standard of 50 parts-per-trillion (ng/L). Virginia is the only state in the nation with a discharge standard for TBT. Some Virginia shipyards now operate under Consent Order deadlines, which mandate compliance with the 50 ng/L discharge limit by December 2001.

The adoption of this standard has had a major impact on the Virginia ship repair industry. Shipyards generate TBT water from wash-down operations in dry-docks where fresh water is used to remove salt and slime from ship's hulls. This operation must be performed on all dry-docked ships. TBT levels in process waters from ship wash-down have been observed to be approximately 10,000 times higher than the new Virginia discharge standard. TBT is also generated from repair operations on sonar domes of US. Navy surface combat ships.

Background

Between 70 and 75% of the 27,000 deep water commercial ships have hulls coated with an antifouling paint containing TBT. These paints are used because they are extremely effective for preventing marine growth on the

[1] President and CEO, Advanced Technology Research Project Corporation, P.O. Box 2439, Falls Church, VA 22042, Tel. (703) 237-0505, Fax (703) 241-1278, E-Mail: machamp@aol.com
[2] Associate Professor, Old Dominion University, Civil Engineering, Kaufman Engineering Hall, Room 130, Norfolk, VA 23529, Tel. 757-683-4673, Fax. 757-683-5354, gschafra@odu.edu
[3] Executive Director, Center for Advanced Ship Repair and Maintenance (CASRM), Norfolk, VA, Tel. (757) 622-2137, Fax (757) 622-2490, E-Mail: casrm@infi.net

hulls, which can reduce ship speed and increase fuel costs. TBT is highly toxic to aquatic life at very low concentrations measured in parts-per-trillion (ng/L), see Champ and Seligman (1996).

The largest source of TBT in coastal US marine waters is that leached from the hulls of the thousands of ships which visit the US ports each year to load and unload cargo. This discharge is designated as non-point source and is unregulated in the United States.

A second and lesser source (but is a point source) of TBT from ships to the marine environment is when ships are dry-docked for standard hull inspection and certification (for insurance purposes) and or repair. The first operation in dry-dock is to wash down hoses the hull with high-pressure fresh water in order to remove marine salt and slime. This operation must be done to permit inspection of the hull and coatings, and in preparation for any hull repair work. A typical wash down job may generate over 100,000 gallons of wash wastewater, containing varying amounts of TBT from several thousand to several hundred thousand parts-per-trillion.

Virginia is the first state in the country to incorporate a numerical TBT limit for Virginia Pollution Discharge Control System (VPDES) shipyard permits. A consent order has been signed between the parties (DEQ, EPA and Shipyards) involved to meet a deadline of December 1, 2001 for Virginia shipyards for compliance with discharging water containing less than 50 ng/L of TBT. However, Newport News Shipbuilding has in its permit, compliance by June 4th, 2000.

Removing pollutants from industrial waste streams is fairly straightforward at levels of parts per million, It is much more difficult and expensive at levels of parts per billion. Purifying large quantities of water to levels of parts per trillion is a major technical challenge. At present, shipyards have no practical guidance on any technology that can be employed to meet regulatory discharge limits.

Over a period of 40 years, TBT has been the subject of many hundreds of studies that have documented the effects of TBT on different marine organisms(in different bodies of water). The effects of pH, water temperature, salinity and seasons of the year have been measured, as have the rate of decay of TBT in the environment, the fate of TBT in sediments, etc. Four international Symposia have been held related to fate and effects of TBT in the marine environment and a reference work has been published from some 40 years of studies (Champ and Seligman, 1996).

Notably missing from this body of knowledge is any work relating to the removal of TBT from industrial waste streams. There are a small number of papers relating to the fate of TBT in municipal wastewater plants using activated sludge (Fent 1996), but this involved low concentrations of TBT (200 ng/L) in the influent water stream. Industrial waste streams from shipyards have measured TBT levels as high as 480,000 ng/L, which is known to be sufficient to kill the bacteria in activated sludge (Argaman *et al*, 1984). Additionally, water from dry-dock wash-down operations is intermittently generated, which rules out biological processes as a viable treatment option.

There is very little published information concerning the treatment of TBT in wastewater. Shipyards have no guidance on how to treat their water to remove TBT.

Virginia Shipyards' Approach to Achieving TBT Compliance

Virginia shipyards elected to work together cooperatively to address the TBT compliance challenge. Several years ago the shipyards helped establish the Center for Advanced Ship Repair and Maintenance (CASRM) as a cooperative partnership between the industry and the College of Engineering and Technology at Old Dominion University, Norfolk, VA. The CASRM consortium has since coordinated most of the shipyards TBT research, development and demonstration projects.

CASRM first commissioned a global bibliography of scientific papers (Alden et al., 1996) dealing with the adverse ecological effects of TBT. This bibliography detailed over 600 different scientific studies that defined the extent of the problem; however, there was virtually no information in the published work that could give guidance to shipyards on how to treat TBT in wash down wastewaters.

In 1997, CASRM began a project to determine the state-of-the-art technological practices regarding the reduction of TBT concentrations in wastewater (Messing et al, 1997). The National Shipbuilding Research Program (NSRP) funded this project. A survey was made of shipyards, researchers, manufacturers of TBT, industries that incorporate TBT into their products, state and federal regulatory agencies, and Regional Water Control Boards, to gain information concerning TBT disposal in waste streams.

The purpose of this study was to identify practical technologies that could be used by shipyards to remove TBT from large volumes of water to levels below 50 ng/L. This study was based on: (1) a review of scientific and engineering literature, (2) a review of U.S. Patents, and (3) a survey of manufacturers and industrial users. The study concluded:

- **There is no "off-the-shelf" technology directly applicable to shipyard waste streams that will reduce TBT levels in water below a concentration of 50 parts per trillion.**

- **Because TBT is highly attracted to particles in water, adsorption process may prove be the most effective means to reduce TBT concentration. It is suggested that technology such as Dissolved Air Floatation, and Activated Carbon Adsorption are the best candidate technologies.**

Also in 1997, in the absence of any available technology, Norfolk Shipbuilding and Drydock Corporation (NORSHIPCO), a member of the CASRM consortium, decided to determine how much progress could be made toward meeting the <50 ng/L goal using different types of standard (off the shelf) water treatment equipment. Subsequently, NORSHIPCO assembled a small industrial water treatment processing plant to conduct some preliminary studies to treat the washdown wastewater using equipment leased on a trial basis. The equipment was not properly sized for the water flow, nor was it used in an optimum way. The results were, however, sufficiently encouraging that water treatment was repeated on a series of subsequent TBT jobs, using variations of equipment to try different alternatives.

Summary of Treatment Studies at NORSHIPCO, 1997 and 1998

These studies were conducted on a large floating dry-dock having a smooth cambered deck on which heavy machinery could be easily relocated. With this kind of dry-dock, ballast tanks are flooded to sink the dock, the ship to be repaired is floated into the dock, and air is pumped into the tanks to raise the dock and the ship out of water. The average size of vessels included in this study was approximately 800' long and 100' wide, and having an underwater hull area in excess of 100,000 square feet.

Washdown is the first operation to be initiated as soon as the ship is out of the water. Typically this is done manually, using a crew of about 20 laborers, and continues through several shifts for a total of about 30 hours. Each operator uses a moderate pressure water washer, using fresh water only at a rate of 4 gpm. Typical water usage on this job is 140,000 gallons. The washdown serves to remove three materials from the hull: sea salt, a wet marine slime, which has the texture and appearance of dead algae, and the top layer of antifouling paint.

After washdown, the hulls of all the ships in this study were inspected, and in every case were found to be in excellent shape with little or no damage from corrosion or marine growth. This is testimony to the efficacy of modern TBT antifouling paints. Washwater was collected by ballasting the dock in order to tilt it slightly, so that all the washwater drains to one end, where it was collected in troughs on the apron of the deck. From here the water was pumped to holding tanks to await treatment.

Figure 1 provides a flow diagram for the experimental treatment system that has been developed following the NORSHIPCO experimental water treatment studies in 97 and 98. The equipment used in the NORSHIPCO studies included: (1) Dissolved Air Floatation to remove suspended solids, (2) a sand filter to remove fine suspended solids and (3) an activated carbon bed to remove dissolved organic materials including TBT. These technologies have been included in the design of the CASRM Barge Treatment System and Process Train, see Figure 1 below.

Water samples were sent to a commercial laboratory for analysis of TBT concentration and toxicity. TBT concentrations in different water samples collected from different treatment steps over time as ship washdown wastewaters were being treated is presented in Table 1.

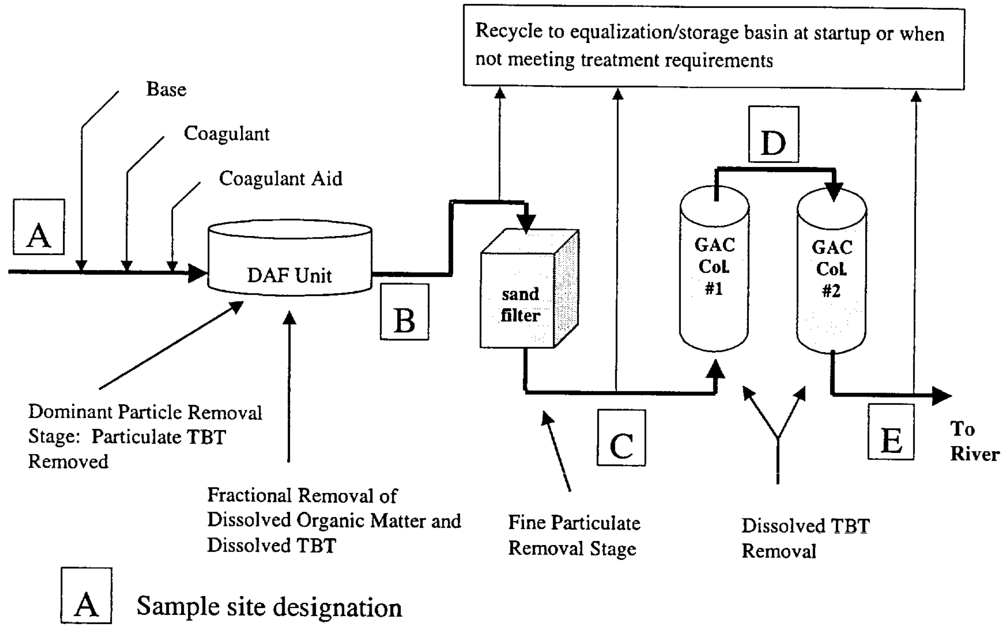

Figure 1. Schematic of the 1999 CASRM Barge Treatment Plant SYSTEM and Process Train for TBT Removal.

Table 1. Test results to remove TBT from shipyard wash water during 1997. Data courtesy of NORSHIPCO, Norfolk, VA.

Ship	*Equipment Sequence*	*Treatment Stage*	*TBT Levels (ng/L)*
Fascination	*DAF; Carbon(1)*	*Pre Carbon*	*180,000*
4/29-30/97		*Post Carbon*	*310*
		Post Carbon	*210*
		Post Carbon	*2,140*
MV Po Hang Yu	*DAF; Sand; Carbon (1)*	*Trough*	*8,300*
7/2/97		*Pre DAF*	*11,000*
		Pre Carbon	*8,500*
		Post Carbon	*70*
		Post Carbon	*69*
Zealand Expedition	*DAF; Sand; Carbon (1)*	*Pre DAF*	*8,100*
8/2/97		*Pre Carbon*	*8,000*
		Post Carbon	*790*
Inspiration	*DAF; Sand; see text*	*Pre DAF*	*485,000*
9/12/97		*Post Carbon*	*18,000*
		Post Carbon	*41*
		Post Carbon	*210*
Ecstasy	*DAF; Sand; Carbon (1)*	*Post Carbon*	*540*
1/30/98			

The first set of data for the cruise ship Fascination found that the TBT concentration prior to passing through the carbon bed was 190,000 ng/L. TBT levels in wash water from all ships prior to passing through carbon absorbent varied from 8,300 ng/L to 480,000 ng/L. This may reflect different levels of TBT in different types of paint.

Activated carbon is very effective in removing dissolved TBT from water. The data from the Inspiration is particularly striking. The concentration of TBT in the water stream was reduced from 480,000 ng/L to 41 ng/L by passing it through the carbon bed. This level would meet the Virginia discharge limit goal of 50 ng/L. The key to effective TBT removal by carbon is effective removal of suspended solids by earlier stages, and providing for sufficient volume of carbon to handle the adsorption load.

It should be recognized that carbon would adsorb nearly all organic material presented to it, so it is important to reduce the presence of other organic contaminants in wastewaters as much as possible. Adsorption is a surface area phenomenon. As carbon adsorbs organic material, there is less surface area left and its adsorption efficiency drops as it becomes exhausted. Previous work by CASRM on storm water runoff from a dry-docks suggests that non-TBT dissolved organic material may be several orders of magnitude higher than TBT concentration.

Over the five ship series, the TBT removal rate varied from 90% to 99.99%. On one occasion, the goal of <50 ng/L was achieved, but 12 hours later performance had dropped to 210 ng/L.

These tests at NORSHIPCO demonstrated the potential of a carbon based system to be able to remove TBT from wastewaters to below 50 ng/L, and focused attention on areas where further R&D was needed. A major concern was to refine and make the process more efficient and cost effective and to reduce the amount of carbon utilized and total waste residue.

The equipment utilized in the NORSHIPCO studies was not optimum; they were chosen because they were available off the shelf at the time. The DAF was rated at 25 GPM, but in order to keep up with shipyard production schedule, it was operated at rates up to 60 GPM. In addition the DAF was optimized for removal of metals (zinc and copper), not removal of TBT. The carbon bed was also severely undersized for the water throughput used.

Another difficulty experienced during these studies was the time delay between submitting water samples and receiving TBT analysis results. The commercial laboratory chosen routinely required three weeks to report TBT numbers. In many cases, the ship had left dry-dock before TBT levels in the water samples were known. Enquiries with various laboratories revealed that TBT analysis at levels of parts per trillion is very complicated, labor intensive, and expensive at these levels. In a laboratory set up to perform TBT analysis routinely, a minimum of two days is required per sample.

It became clear during these tests that a much faster (shorter time period) method for analyzing the water effluent was required. During the shipyard tests, the equipment was set up and operated during the wash-down without any real time knowledge of the TBT level in the effluent. A rapid method to assess TBT concentration is needed for treatment system process control.

The initial process investigated was coagulation and precipitation. Water collected from a wash down of a cruise ship in October 1999, was used for this study. This water had a TBT level of over 1.1 million parts per trillion (pptr) of TBT, which is the highest ever measured in the course of this project. The initial lab work involved the addition of different types of coagulant, different quantities of coagulation, combined with different pH levels. Best results were obtained at pH 6 using 50 mg of alum/liter. Under these conditions untreated water contained 1.1 million pptr, and the resulting effluent after treatment was 6,000 pptr a reduction of 99.4%.

The second process investigated was adsorption by activated carbon. Using batch processing it has been determined that TBT concentrations can be reduced from thousands of pptr to less than 6 pptr (the limit of detection of the ODU analytical technique). Carbon adsoption, also pH dependant displays an optimum in the 6-8 pH range. Figure 2. below presents a summary of results of laboratory treatment by coagulation and adsorption on a shipyard wash water sample.

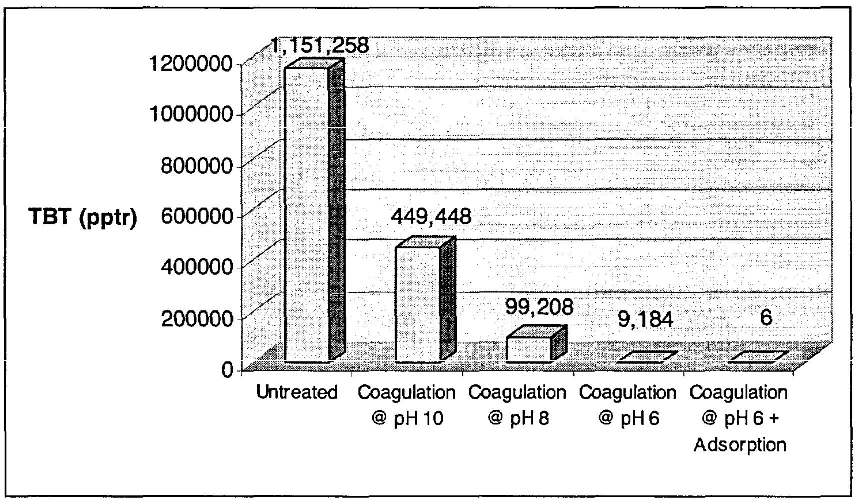

Figure 2. Treatment of Shipyard Wash Water - Dissolved TBT Remaining after Coagulation with 60 mg/L Alum and Carbon Adsorption at Different pH Levels

UK (Ashcroft and Able, 1999) Method

The development, testing and commercialization of this technology has been over a ten year period:

1991 University of Sunderland proposal
1992 EC MEDSPA support
1995 Pilot scale process demonstrated
1996 Joint-venture formed for scale-up
1997 $10te.hr^{-1}$ system proved

The extraction process is carried out by dispersion of an appropriate solvent in the process water stream. The dispersion provides an environment for mass transfer of the target species into the extraction phase (solvent). To achieve this end the solvent is dispersed to form a high surface area to enable mass transfer to take place. Once the extraction process is complete the solvent dispersion is coalesced for post-extraction treatment of the waste stream.

The development includes a patented process for development and maintenance of a large surface area at which interface the mass transfer takes place. The final part of the process involves the coalescence of the dispersed phase for separation and recovery / disposal of the target pollutant.

The new consortium expects to have a laboratory / pilot installation available early in 2000. This will be used to further evaluate performance and design the commercial units to be made available later in 2000.

The consortium objectives are to promote and exploit the technology because of what are seen as substantial process benefits. These are clearly apparent when the process is compared to alternative technologies applied to TBT and similar water treatment problems.

The benefits of this technology include:

a) minimization of waste volume;
b) no generation of solid waste;
c) avoidance of civil works;
d) design as a mobile, modular system;
e) parallel operation with waste production;
f) elimination of need for process water storage;
g) minimization of operating costs;
h) adaptability for future changes in standards;
i) applicability to other pollutant streams; and
j) robust construction for industrial operation.

A major benefit is a massive volume reduction in terms of the waste stream from the process. The operating parameters require a solvent volume amounting to between 2 and 4% of the process mass. If a nominal $10te.hr^{-1}$ is processed during a 10-hour period 100te of process water will be treated. The hold up volume of the system pipe work will be some hundreds of liters. This gives an average requirement substantially below 100 liters of extraction fluid. The external hold up volume where post processing of the extraction fluid may take place could lead to a parallel solvent reservoir of perhaps 200 liters to allow for any secondary processing. This will not necessarily change even if the unit is operated continuously for days or weeks.

In practice it has been identified that a wide range of oils are suitable as extraction solvent. It may be acceptable locally to use an existing waste oil stream to effectively avoid creation of an additional waste stream.

The process is viewed as a series of separate modules. The individual components are illustrated in the schematic presented in Figure 1. The first module [1] includes a transfer pump to take the process stream from the source and will include primary screening to remove solids etc. The front end of the process unit will have a reservoir [2] to allow priming of the system prior to initiating treatment. This primary fluid stream will then be pumped [3] to the "reactor pipe work" [4]. A controlled fraction of the main flow is diverted [5] to the dosing system [6]. In this module
a concentrate is made with the extraction solvent being dispersed in the process liquid. The system will be capable of admitting any extraction solvent appropriate to the target pollutant.

The "reaction" module [4] maintains the dispersion of extraction solvent while the pollutant is extracted. The treated mixture then enters the separation module [7] where the solvent and cleaned water streams are separated. The water can go for discharge [8] or "polishing" [9] according to local quality standards. The oil stream is collected [10] for reuse, treatment or disposal according to local requirements. The solvent collection module can include secondary processing, recycling or simple discharge facilities.

Prototype Performance

The technology has been proven to operate in an industrial environment with the ability to reduce TBT levels from $2mg.l^{-1}$ to $200ng.l^{-1}$. The use of repeat extraction modules will give progressive further reduction with no effective increase in waste volume produced. The estimated cost for each metric tonne of effluent treated is £4 (<$7).

Acknowledgements

This project has been funded by the Office of Naval Research, Arlington, Virginia. Dr. Hal Guard and Dr. Alex Lardis have been the Program Officers.

References Cited

Alden III, R.W., R.J. McDanie II, T.A. Ribeiro, L.M. Ramirez, J.H. Rose. 1996. A Literature Search for the Effects of Tributyltin on Aquatic Organisms and Current Tributyltin on Aquatic Organism and current Tributyltin Regulatory Limits Among Regulatory States of the United States. TR. No. 3008. Applied Marine Research Laboratory. Old Dominion University, Norfolk, VA 23529-0456. 157p.

Argamen, Y., Hucks, C.E. and S.E Shelby. 1984. The Effects of Organotin on the Activated Sludge Process. *Water Research.* **18**(5): 535-542.

Ashcroft, Peter L. and David Abel. 1999. Process Water Treatment for the Removal of TBT in Ship Washdown Waste Waters. Proceedings Marine Technology Society. Washington, D.C. Vol. 5, 12 P.

Champ, M.A. and P.F. Seligman. (Eds). 1996. *Organotin, Environmental Fate and Effects.* Chapman and Hall. London. 674p.

Champ, M.A., G.C. Schafran, T.J. Fox, G.A. Cutter, M. Unger, and G. Salata. 1999. Quality Assurance Project Plan for the Analysis and Treatment of TBT in Waste Waters from Virginia Shipyards and Drydocks. CASRM. Norfolk, Virginia. 170p.

de Mora, S.J., C. Stewart and D. Phillips. 1995. Sources and Rate of Degradation of Tributyltin in Marine Sediments Near Aukland, New Zealand. *Marine Pollution Bulletin,* **30**(1):50-57.

Fent, K. 1996. Organotin Compounds in Municipal Wastewater and Sewerage Sludge: Contamination, Fate in Treatment Process and Ecotoxicological Consequences. *The Science of the Total Environment.* **185**:151-159.

Grovhoug, J.G., P.F. Seligman, G. Vafa, and R.L Fransham. 1986. Baseline Measurements of Butyltin in U.S. Harbors and Estuaries. *Oceans '86, Vol 4, Organotin Symposium,* Washington D.C. Vol. 4:1283-1288

Messing, A.W., L.M. Ramirez and T.J. Fox. (1998). A Review to Determine State-of-the-Practice Treatment Technologies for Reducing Concentrations of Organotin Compounds in Wastewater. *National Shipbuilding Research Program Report.* Ann Arbor Michigan. 57p.

Page, D.S., C.C. Ozbal and M.E. Lamphear. 1996. Concentration of Butyltin Species in Sediments Associated with Shipyard Activities. *Environmental Pollution.* **81**(2):237-243.

Seligman, P.F. (1984) "Fate and Effects of Organotin Antifouling Leachates in the Marine Environment." Bethesda, MD.